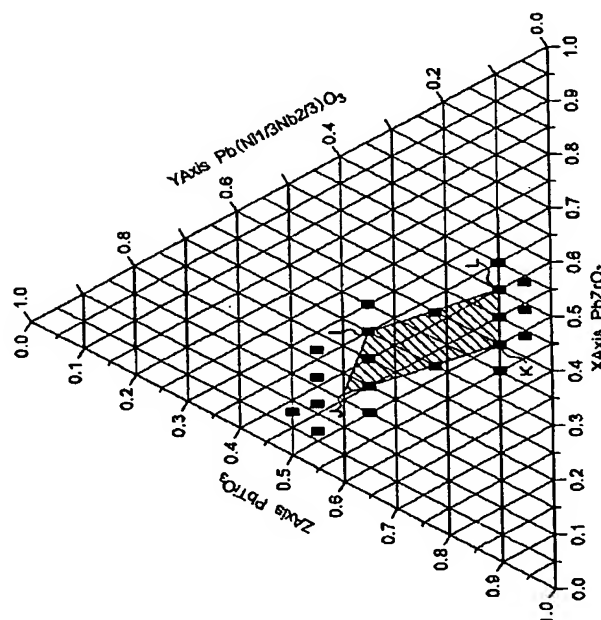(54)【発明の名称】　圧電磁器組成物

(57)【要約】

【課題】　高電界下での圧電変位量が大きく，且つ比誘電率の温度変化が小さいとともに，絶縁性に優れた圧電磁器組成物を提供する。

【解決手段】　圧電磁器組成物は、組成式 $aPbTiO_3 + bPbZrO_3 + cPb(Ni_{1/3}Nb_{2/3})O_3$（a＋b＋c＝100）で表され，その組成範囲が，I点（a＝35mol%，b＝30mol%，c＝35mol%），J点（a＝44mol%，b＝16mol%，c＝40mol%），K点（a＝50mol%，b＝40mol%，c＝10mol%），及びL点（a＝40mol%，b＝50mol%，c＝10mol%）の組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分とし，d33を向上させるため，Pb成分量の調整，副成分を添加した組成からなる。

【特許請求の範囲】
【請求項1】 組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$ $(a+b+c=100)$ で表され、その組成範囲が、図1のI点 $(a=35mol\%,\ b=30mol\%,\ c=35mol\%)$、J点 $(a=44mol\%,\ b=16mol\%,\ c=40mol\%)$、K点 $(a=50mol\%,\ b=40mol\%,\ c=10mol\%)$、およびL点 $(a=40mol\%,\ b=50mol\%,\ c=10mol\%)$ の各組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分とし、Pb量を $0\sim3mol\%$（0を除く）の範囲で減少させた、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、-40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器組成物。

【請求項2】 請求項1記載の圧電磁器組成物において、母成分に対してLa、Nd等のランタノイド元素およびSr等のアルカリ土類元素のうち少なくとも1種を $0\sim7mol\%$（0を除く）の範囲で添加し、かつPb量を $0\sim5mol\%$（0を除く）の範囲で減少させた、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器組成物。

【請求項3】 組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$ $(a+b+c=100)$ で表され、その組成範囲が、図1のI点 $(a=35mol\%,\ b=30mol\%,\ c=35mol\%)$、J点 $(a=44mol\%,\ b=16mol\%,\ c=40mol\%)$、K点 $(a=50mol\%,\ b=40mol\%,\ c=10mol\%)$、およびL点 $(a=40mol\%,\ b=50mol\%,\ c=10mol\%)$ の各組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分とし、La、Nd等のランタノイド元素およびSr等のアルカリ土類元素のうち1種類以上を $0\sim5mol\%$（0を除く）の範囲で添加した、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、-40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器組成物。

【請求項4】 請求項1乃至3の内のいずれかに記載の圧電磁器組成物において、総量に対して、MnをMnOで表される酸化物に換算して、 $0\sim0.05wt\%$（0は含まない）の割合で含有し、-40℃～170℃における比抵抗が $1.0／10^{11}\Omega\cdot cm$ 以上であることを特徴とする圧電磁器組成物。

【発明の詳細な説明】
【0001】
【発明の属する技術分野】本発明は、チタン酸ジルコン酸鉛を主成分とする圧電磁器組成物に関するものであり、特に高電界下での圧電変位量が大きく、且つ比誘電率の温度変化が小さいとともに、絶縁性に優れた圧電磁器組成物に関するものである。

【0002】
【従来の技術】従来、圧電磁器材料としては、 $PbTiO_3$ や $PbZrO_3$ を主成分として含む圧電セラミックス（以下、PZT系圧電セラミックスと呼ぶ）や、複合ペロブスカイト類を第三、第四成分として固溶させた多成分系PZT系圧電セラミックスが、圧電定数が大であるために、圧電振動子を初めとしてアクチュエータ用の材料として広く利用されている。

【0003】これらの系の材料は、一般にモルフォトビック相境界（MPB）近傍組成において、圧電定数（d定数）等の圧電変位に寄与する特性が向上するため、アクチュエータ用材料としては、前記MPB近傍組成の圧電磁器材料が広く実用化されている。

【0004】
【発明が解決しようとする課題】しかしながら、前記圧電定数は一般にEMAS-6100等で示された、共振-反共振法で求められた値であり、基本的には低電界（約数百V／m程度）印加時の圧電変位の割合を示している。これに対し、実際の圧電アクチュエータにおける駆動電界は、数百kV／m～数千kV／mにもなり、前記方法で求めた圧電定数が実用的な意味を持たない場合がある。さらに、近年圧電アクチュエータ利用範囲の広がりに伴い、広い温度範囲での特性安定性、特に静電容量の温度安定性が求められている。例えば、自動車用部品として圧電アクチュエータが使用される場合には、その使用環境に応じて、-40℃～170℃にもなる広い温度範囲での特性安定性が要求される場合がある。これに対し、一般に前記MPB近傍組成での圧電磁器材料は、比誘電率の温度変動が大きくなり、広い温度範囲におけるアクチュエータ特性の安定性、特に静電容量の安定性に問題が生じている。

【0005】 $PbTiO_3-PbZrO_3-Pb(Ni_{1/3}Nb_{2/3})O_3$ 系（以下、PNN-PZT系と呼ぶ）の圧電磁器組成物はd定数が大きいため、アクチュエータ素子用の圧電磁器材料として利用されている。

【0006】しかし、圧電アクチュエータの応用範囲が広がるにつれ、さらに大きなd定数を持つ材料が求められている。また、この系の圧電磁器材料は電気抵抗率が比較的小さく、積層型圧電素子のように、一層の厚みが100μm前後の素子に使用した場合、印加できる電圧を大きくできず、充分な特性を引き出せなかったり、使用中に絶縁破壊してしまう等の問題点が生じている。

【0007】また、前記PNN-PZT系圧電磁器材料は、電気抵抗率の温度変動も大きいため、特に前述のような広い温度範囲で使用する場合には、さらに信頼性が低下するなどの問題があった。

【0008】そこで、本発明の一技術的課題は、高電圧印加時の圧電歪定数が大きく、かつ、比誘電率の温度変化が小さく、高温度範囲での電気抵抗率も大きく、したがって、広い温度範囲で安定な特性を有するとともに絶縁性に優れた圧電磁器組成物を提供することにある。

【0009】また、本発明の特別な技術的課題は、アクチュエータ用材料として極めて有用な圧電磁器組成物を提供することにある。

【0010】
【課題を解決するための手段】本発明者は、組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$（a+b+c＝100）で表される圧電磁器組成物の圧電変位特性を種々調査した結果、その組成範囲が所定の領域にあり、Pb量を減少させることや、La，Nd等のランタノイド元素およびSr等のアルカリ土類元素を副成分として添加する事で分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位（以下、d33（500kV））が母成分のみの場合より改善し、かつ、－40℃～170℃の範囲における比誘電率の温度変化の劣化が少ない圧電磁器組成物を見いだした。また、上記記載の圧電磁器材料に対して、MnをMnOで表される酸化物に換算して、0～0.05wt％（0は含まない）の割合で含有することにより、圧電磁器組成物の絶縁性が向上することを見出し、本発明を為すに至ったものである。

【0011】即ち、本発明によれば、組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$（a+b+c＝100）で表され、その組成範囲が、図1のI点（a＝35mol％，b＝30mol％，c＝35mol％）、J点（a＝44mol％，b＝16mol％，c＝40mol％）、K点（a＝50mol％，b＝40mol％，c＝10mol％）、およびL点（a＝40mol％，b＝50mol％，c＝10mol％）の各組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分とし、Pb量を0～3mol％（0を除く）の範囲で減少させた、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、－40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器組成物が得られる。

【0012】また、本発明によれば、前記圧電磁器組成物において、母成分に対してLa，Nd等のランタノイド元素およびSr等のアルカリ土類元素のうち少なくとも1種を0～7mol％（0を除く）の範囲で添加し、かつPb量を0～5mol％（0を除く）の範囲で減少させた、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器

組成物が得られる。

【0013】また、本発明によれば、組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$（a+b+c＝100）で表され、その組成範囲が、図1のI点（a＝35mol％，b＝30mol％，c＝35mol％）、J点（a＝44mol％，b＝16mol％，c＝40mol％）、K点（a＝50mol％，b＝40mol％，c＝10mol％）、およびL点（a＝40mol％，b＝50mol％，c＝10mol％）の各組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分とし、La，Nd等のランタノイド元素およびSr等のアルカリ土類元素のうち1種類以上を0～5mol％（0を除く）の範囲で添加した、分極軸と同一方向に、500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、－40℃～170℃の範囲で、比誘電率の温度変化が300％以下であることを特徴とする圧電磁器組成物が得られる。

【0014】また、本発明によれば、前記いずれかの圧電磁器組成物において、総量に対して、MnをMnOで表される酸化物に換算して、0～0.05wt％（0は含まない）の割合で含有し、－40℃～170℃における比抵抗が $1.0×10^{11}Ω・cm$ 以上であることを特徴とする圧電磁器組成物が得られる。

【0015】
【発明の実施の形態】まず、本発明の圧電磁器組成物について図面を参照しながら説明する。

【0016】図1は本発明の圧電磁器組成物の母成分の組成を三角座標で示す図である。

【0017】本発明の圧電磁器組成物は、組成式 $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$（a+b+c＝100）で表され、その組成範囲が、図1のI点（a＝35mol％，b＝30mol％，c＝35mol％）、J点（a＝44mol％，b＝16mol％，c＝40mol％）、K点（a＝50mol％，b＝40mol％，c＝10mol％）、およびL点（a＝40mol％，b＝50mol％，c＝10mol％）の各組成点を結ぶ線上およびこの4点に囲まれた領域とする範囲を母成分としている。

【0018】本発明の圧電磁器組成物の一例は、この母成分からPb量を0～3mol％（0を除く）の範囲で減少させることによって、分極軸と同一方向に500kV／mの直流電界を印加したときの圧電変位が、500pm／V以上を示し、かつ、－40℃～170℃の範囲で、比誘電率の温度変化が300％以下とした圧電磁器組成物である。

【0019】また、本発明の圧電磁器組成物のもう一つの例は、前記圧電磁器組成物において、母成分に対してLa，Nd等のランタノイド元素およびSr等のアルカリ土類元素のうち少なくとも1種を0～7mol％（0

を除く）の範囲で添加し、かつPb量を０～５mol％（０を除く）の範囲で減少させることによって、分極軸と同一方向に、５００kV／mの直流電界を印加したときの圧電変位が、５００pm・V以上を示し、かつ、４０℃～１７０℃の範囲で、比誘電率の温度変化が３００％以下とした圧電磁器組成物である。

【００２０】また、本発明の圧電磁器組成物のさらにもう一つの例は、前記母成分に、Ｌａ、Ｎd等のランタノイド元素およびＳr等のアルカリ土類元素のうち１種類以上を総量に対して０～５mol％（０を除く）の範囲で添加することによって、分極軸と同一方向に、５００kV／mの直流電界を印加したときの圧電変位が、５００pm／V以上を示し、かつ、－４０℃～１７０℃の範囲で、比誘電率の温度変化が３００％以下である圧電磁器組成物である。

【００２１】また、本発明の圧電磁器組成物の別の例は、前記母成分に対して、Ｌａ、Ｎd等のランタノイド元素およびＳr等のアルカリ土類元素のうち少なくとも１種を総量に対して０～７mol％（０を除く）の範囲で添加するとともに、Pb量を０～５mol％（０を除く）の範囲で減少させることによって、分極軸と同一方向に、５００kV／mの直流電界を印加したときの圧電変位が、５００pm／V以上を示し、かつ、４０℃～１７０℃の範囲で、比誘電率の温度変化が３００％以下である圧電磁器組成物である。

【００２２】また、本発明の圧電磁器組成物の他の例は、前記いずれかの圧電磁器組成物において、総量に対して、ＭnをＭnＯで表される酸化物に換算して、０～０．０５wt％（０は含まない）の割合で含有させたものであり、－４０℃～１７０℃における比抵抗が１．０×10^{11}Ω・cm以上である圧電磁器組成物である。

【００２３】それでは、本発明の実施の形態について説明する。

【００２４】（第１の実施の形態）酸化チタン（ＴiＯ$_2$）、酸化ジルコニウム（ＺrＯ$_2$）、酸化ニッケル（ＮiＯ）、酸化ニオブ（Ｎb$_2$Ｏ$_5$）の原料とPb量減少させた酸化鉛（PbＯ）を目標組成となるように秤量し、これらの原料粉をジルコニアボールとともにアクリルポット中に入れ、２０時間湿式混合した。

【００２５】次に、これらの混合粉を脱水乾燥後、アルミナこう鉢中で予焼を行ってから、各予焼粉をアクリルポット中ジルコニアボールにて１５時間湿式粉砕した。引き続き、脱水乾燥して得られた予焼粉砕粉にバインダを混合して加圧し、直径（φ）２０×厚み（Ｔ）３mmに成形した。この成形体を１１００℃～１３００℃で２時間焼成し、各焼結体を１mmの厚さに加工した後、両面に銀ペーストを塗布して４５０℃で焼き付けて電極を形成することにより、それぞれ組成の異なる試料とした。このようにして得られた各試料を３kV／mm、で分極処理をし、ＨＰ４１９４Ａと恒温槽を使用して、１

kHzの比誘電率εrの温度特性を測定した。温度特性は、－４０℃～４００℃の範囲で５℃～１０℃毎に３０分保持したのち、各温度での１KHzのεrを測定した。また、d33（５００kV）は、中心点で支持した前記試料に、等速、２秒間で０V→５００V→０Vの電圧を印加し、試料厚さ方向の変位をフリンジカウンタ式レーザ変位計を使用して測定して算出した。

【００２６】図２は、d33（５００kV）の測定例を示す図である。図２に示すように、厚さ１mmの測定試料に、５００Vの直流電圧印加時（電界強度５００kV／m）の変位量からd33（５００kV）を算出した。

【００２７】また、下記表１、２の試料１～２６に母成分とPb減少材料のd33（５００kV）と－４０℃～１７０℃でのεrの温度変化率を示す。表中、＊のついた試料Ｎo．は、本発明の範囲外を示している。

【００２８】上記表１より、以下の事が読み取れる。すなわち、Pb量を減少することで温度特性を維持しつつd33（５００kV）の向上が認められる。d33（５００kV）の向上はPb減少量が１．５mol％程度をピークとして徐々に低下する。Pb減少量が過剰になると試料の焼結性が低下しはじめ、焼結温度の高温化、試料の特性劣化が生じ好ましくない。試料Ｎo．２５、２６は、それぞれd33（５００kV）の値が、５００pm／V未満となるため、本発明の範囲に含まれない。これらの結果から、本発明の目標とする特性は、Pb減少量が０～３mol％（０は除く）の範囲で達成されることがわかる。

【００２９】（第２の実施の形態）酸化鉛（PbＯ）、酸化チタン（ＴiＯ$_2$）、酸化ジルコニウム（ＺrＯ$_2$）、酸化ニッケル（ＮiＯ）、酸化ニオブ（Ｎb$_2$Ｏ$_5$）の母成分原料と添加物元素として酸化ランタン（Ｌa$_2$Ｏ$_3$）、酸化ネオジウム（Ｎd$_2$Ｏ$_3$）、炭酸ストロンチウム（ＳrＣＯ$_3$）を目的組成となるように秤量し、第１の実施の形態と同様に試料を作成、諸特性の評価を行った。

【００３０】下記表１及び表２の試料Ｎo．２７～３９に、添加物試料のd33（５００kV）と、－４０℃～１７０℃でのεrの温度変化率を示す。下記表１及び表２中＊のついた試料Ｎo．は、本発明の範囲外を示している。下記表１より、以下の事が読み取れる。すなわち、各元素共に添加物量の増加に従いd33（５００kV）の向上が認められると共に、Δεrの値が劣化する。過剰にＳrを添加した試料Ｎo．３０はΔεrが３００％を超えているため本請求範囲より除外される。また、試料Ｎo．３９は試料作成中に破損し測定できなかった。

【００３１】（第３の実施の形態）酸化鉛（PbＯ）、酸化チタン（ＺrＯ$_2$）、酸化ジルコニウム（ＺrＯ$_2$）、酸化ニッケル（ＮiＯ）、酸化ニオブ（Ｎb$_2$Ｏ$_5$）の母成分原料と添加物元素として酸化ランタン

（La$_2$O$_3$），酸化ネオジウム（Nd$_2$O$_3$），炭酸ストロンチウム（SrCO$_3$）を目的組成となるように秤量し第1の実施の形態と同様に試料を作成，諸特性の評価を行った。下記表2の試料No.40～64に，試料のd33（500kV）と，−40℃～170℃でのεrの温度変化率を示す。表2中＊のついた試料No.は，本発明の範囲外を示している。下記表2より，以下の事が読み取れる。添加物の添加と共にPb量を減少す

ることで，単純に添加した場合よりも多量の添加物を添加でき，Δεrの劣化が少ない。また，Pb減少量と添加量を加算して0.99mol程度のバランスがとれている試料No.42，47，54等では添加量が比較的少なくても良好なd33（500kV）を示す。

【0032】

【表1】

【表2】

備考	試料No.	各成分 a	b	c	Pb減少量/mol%	添加物	d$_{33}$(500kV)/pm·V^{-1}	Δεr/%
＊	1	43	12	45	−	−	530	500
＊	2	44	16	40	−	−	670	170
＊	3	39	21	40	−	−	1250	650
＊	4	50	15	35	−	−	450	170
＊	5	45	20	35	−	−	530	180
＊	6	40	25	35	−	−	1000	230
＊	7	35	30	35	−	−	800	280
＊	8	30	35	35	−	−	700	700
＊	9	47.5	30	22.5	−	−	520	160
＊	10	37.5	40	22.5	−	−	750	290
＊	11	55	35	10	−	−	470	150
＊	12	50	40	10	−	−	520	160
＊	13	45	45	10	−	−	700	170
＊	14	40	50	10	−	−	600	270
＊	15	35	55	10	−	−	520	700
＊	16	51	44	5	−	−	420	160
＊	17	46	49	5	−	−	480	190
＊	18	41	54	5	−	−	400	280
	19	47.5	30	22.5	0.5	−	714	160
	20	47.5	30	22.5	1	−	811	160
	21	47.5	30	22.5	1.5	−	805	160
	22	47.5	30	22.5	2	−	717	150
	23	47.5	30	22.5	2.5	−	649	160
	24	47.5	30	22.5	3	−	570	170
＊	25	47.5	30	22.5	4	−	306	180
＊	26	47.5	30	22.5	5	−	283	170
	27	43	34.5	22.5	−	1.0mol%Sr	950	210
	28	43	34.5	22.5	−	3.0mol%Sr	1050	220
	29	43	34.5	22.5	−	5.0mol%Sr	1010	270
＊	30	43	34.5	22.5	−	7.0mol%Sr	900	470
	31	43	34.5	22.5	−	0.05mol%Nd	1000	210
	32	43	34.5	22.5	−	0.1mol%Nd	935	200

＊本発明の範囲外

【0033】

備考	試料No.	各成分 a	b	c	Pb減少量/mol%	添加物	d_{33}(500KV)/pm·V⁻¹	Δεr/%
	33	43	34.5	22.5	—	0.3mol%Nd	1150	230
	34	43	34.5	22.5	—	0.5mol%Nd	980	300
	35	43	34.5	22.5	—	0.1mol%La	980	210
	36	43	34.5	22.5	—	0.3mol%La	980	210
	37	43	34.5	22.5	—	0.5mol%La	1080	210
	38	43	34.5	22.5	—	1.0mol%La	860	270
＊	39	43	34.5	22.5	—	2.0mol%La	測定不可	測定不可
	40	43	34.5	22.5	1	0.1mol%La	1050	210
	41	43	34.5	22.5	1	0.3mol%La	1080	230
	42	43	34.5	22.5	1	0.5mol%La	1180	220
	43	43	34.5	22.5	2	0.1mol%La	1000	200
	44	43	34.5	22.5	2	0.3mol%La	1040	220
	45	43	34.5	22.5	2	0.5mol%La	1080	240
	46	43	34.5	22.5	1	0.05mol%Nd	1080	210
	47	43	34.5	22.5	1	0.1mol%Nd	1120	220
	48	43	34.5	22.5	1	0.3mol%Nd	1050	240
	49	43	34.5	22.5	2	0.05mol%Nd	1130	220
	50	43	34.5	22.5	2	0.1mol%Nd	1110	220
	51	43	34.5	22.5	2	0.3mol%Nd	1040	270
	52	43	34.5	22.5	1	1.0mol%Sr	970	200
	53	43	34.5	22.5	1	3.0mol%Sr	1000	210
	54	43	34.5	22.5	2	1.0mol%Sr	1060	210
	55	43	34.5	22.5	2	3.0mol%Sr	1050	220
	56	43	34.5	22.5	2	5.0mol%Sr	1080	260
	57	43	34.5	22.5	3	1.0mol%Sr	1010	200
	58	43	34.5	22.5	3	3.0mol%Sr	1040	210
	59	43	34.5	22.5	3	5.0mol%Sr	1100	270
	60	43	34.5	22.5	4	3.0mol%Sr	1150	210
	61	43	34.5	22.5	4	5.0mol%Sr	1200	260
	62	43	34.5	22.5	5	3.0mol%Sr	1120	210
	63	43	34.6	22.5	5	5.0mol%Sr	1100	250
	64	43	34.5	22.5	5	7.0mol%Sr	1000	300

＊印は本発明の範囲外

【0034】（第4の実施の形態）酸化鉛（PbO），酸化チタン（TiO_2），酸化ジルコニウム（ZrO_2），酸化ニッケル（NiO），酸化ニオブ（Nb_2O_5）の母成分原料と添加物元素として酸化ランタン（La_2O_3），酸化ネオジウム（Nd_2O_3），炭酸ストロンチウム（$SrCO_3$），炭酸マンガン（$MnCO_3$）を目的組成となるように秤量し，第1の実施の形態と同様に試料を作成し，－40℃，170℃それぞれでの比抵抗を測定した。その結果の一例を図3に示す。図3から，恒温領域では比抵抗が低下するものの，MnOとして$MnCO_3$を極微量添加するだけで，比抵抗が顕著に向上し，本発明の目標値を満足することがわかる。また，MnOの添加量は，0.05wt%を超えると，それ以上の比抵抗向上効果は望め無いことがわかった。MnOの過剰な添加は，圧電定数などの圧電特性を劣化させる傾向もあるため，0.05wt%以下が，本発明の目標に対して適当な値であると判断できる。

【0035】
【発明の効果】以上説明したように，本発明においては，高電圧印加時の圧電歪定数が大きく，かつ，比誘電率の温度変化が小さく，高温度範囲での電気抵抗率も大きいことから，広い温度範囲で安定な特性を有するとともに絶縁性に優れた圧電磁器組成物を提供でき、アクチュエータ用材料として極めて有用である。
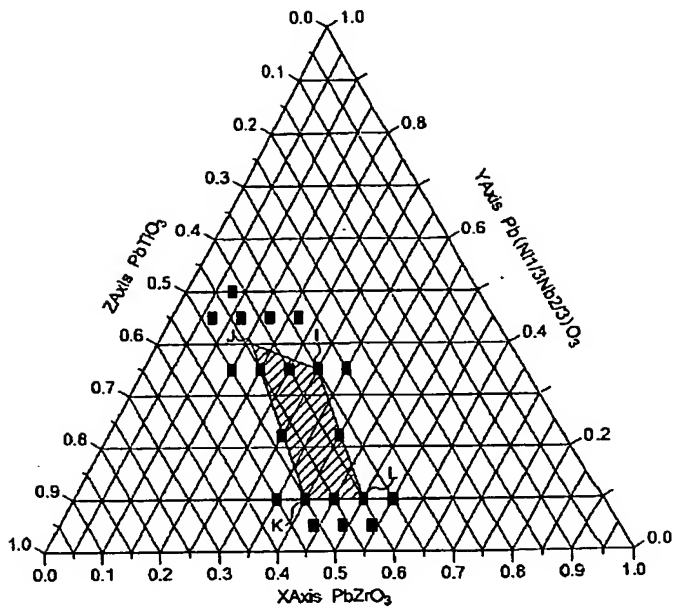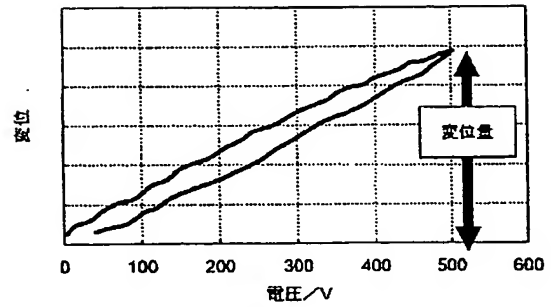
【図面の簡単な説明】
【図1】本発明の圧電磁器組成物の母成分の組成を三角座標で示す図である。
【図2】本発明の第1の実施の形態で示した，d33（500kV）測定方法の概念を示す図であり，印加電圧と圧電変位の関係を示す図である。
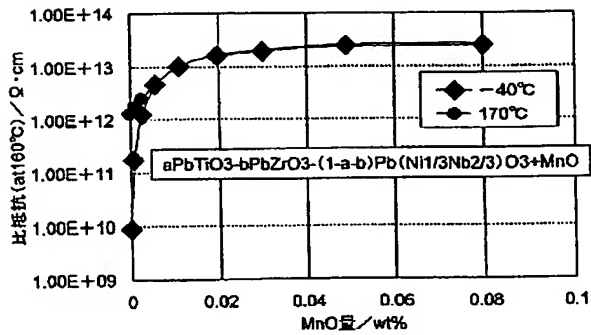【図3】本発明の第4の実施の形態によるMnO添加量と，比抵抗の関係を示す図である。

【図1】

【図2】

【図3】

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(71)Applicant : TOKIN CORP
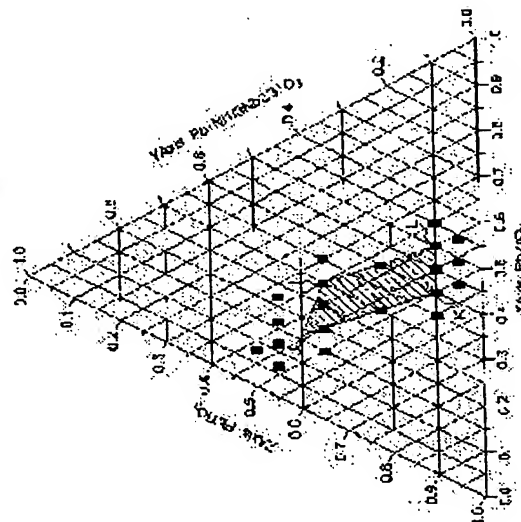TOKIN CERAMICS CORP

(72)Inventor : ISE OSAMU
MAMIYA YOICHI
KAWAKAMI YOSHIHIRO

(54) PIEZOELECTRIC CERAMIC COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a piezoelectric ceramic composition having a large piezoelectric displacement under a high electric field, a small temperature change of a specific dielectric constant and an excellent insulation property.

SOLUTION: The piezoelectric ceramic composition is composed of a mother component, which is expressed by a composition formula, $aPbTiO_3+bPbZrO_3+cPb(Ni_{1/3}Nb_{2/3})O_3$, (a+b+c=100) and exists on a line formed by connecting point I (a=35 mol%, b=30 mol%, c=35 mol%), point J (a=44 mol%, b=16 mol%, c=40 mol%), point K (a=50 mol%, b=4 mol%, c=10 mol%) and point L (a=40 mol%, b=50 mol%, c=10 mol%) and in the region surrounded by the 4 points, in which the Pb content is adjusted and auxiliary components are added to improve d_{33}.

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[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

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PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-302348

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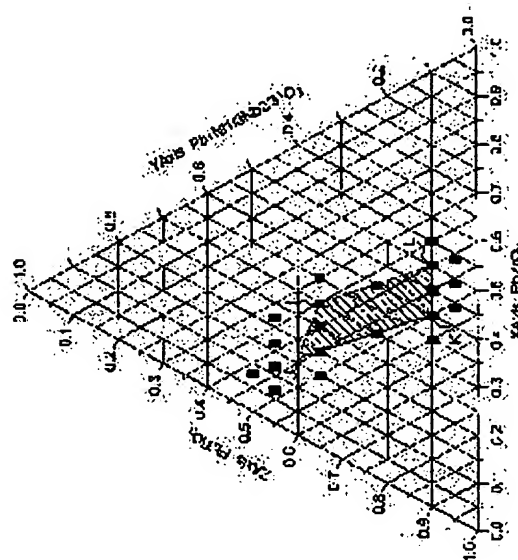|	
(21)Application number : 2000-117437	(71)Applicant : TOKIN CORP TOKIN CERAMICS CORP
(22)Date of filing : 19.04.2000	(72)Inventor : ISE OSAMU MAMIYA YOICHI KAWAKAMI YOSHIHIRO

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CLAIMS

[Claim(s)]
[Claim 1] Empirical formula aPbTiO3+bPbZrO3+cPb (nickel1/3Nb 2/3) It is expressed with O3 (a+b+c=100). The presentation range I points of drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), In the same direction as the polarization shaft which the range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points was used [shaft] as the mother component, and decreased the amount of Pb(s) in [0-3 mol] % (except for 0), and the direct-current electric field of 500 kV/m the piezo-electricity when impressing -- the piezoelectric-ceramics constituent which a variation rate shows 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in the range of -40 degrees C - 170 degrees C.
[Claim 2] In a piezoelectric-ceramics constituent according to claim 1 As opposed to a mother component At least one sort in alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, is added in [0-7 mol] % (except for 0). In **** the amount of Pb(s) in the same direction as **** and a polarization shaft in [0-5 mol] % (except for 0) the direct-current electric field of 500 kV/m the piezo-electricity when impressing -- the piezoelectric-ceramics constituent which a variation rate shows 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in the range of 40 degrees C - 170 degrees C.
[Claim 3] Empirical formula aPbTiO3+bPbZrO3+cPb (nickel1/3Nb 2/3) It is expressed with O3 (a+b+c=100). The presentation range I points of drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), The range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points is used as a mother component. Among alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, and one or more kinds A variation rate shows 500 or more pm/V. the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as the polarization shaft added in [0-5 mol] % (except for 0) -- in -40 degrees C - 170 degrees C The piezoelectric-ceramics constituent characterized by the temperature change of specific inductive capacity being 300% or less.
[Claim 4] The piezoelectric-ceramics constituent which converts Mn into the oxide expressed by MnO, contains it at a 0 - 0.05wt% (0 does not contain) rate to a total amount in claim 1 thru/or a piezoelectric-ceramics constituent given in either of 3, and is characterized by the specific resistance in -40 degrees C - 170 degrees C being 1.0x1011 or more ohm-cm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] the thing about the piezoelectric-ceramics constituent with which this invention uses titanic-acid lead zirconate as a principal component -- it is -- especially -- the piezo-electricity under high electric field -- a variation rate -- while an amount is large and the temperature change of specific inductive capacity is small, it is related with the piezoelectric-ceramics constituent excellent in insulation.
[0002]
[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics ingredient, since a piezoelectric constant is size, the electrostrictive ceramics (it is hereafter called PZT system electrostrictive ceramics) which contains $PbTiO_3$ and $PbZrO_3$ as a principal component, and the multicomponent system PZT system electrostrictive ceramics which made compound perovskites dissolve as the third fourth component are widely used as an ingredient for actuators by making a piezoelectric transducer into the start.
[0003] the ingredient of these systems -- general -- a presentation near the mol photograph pick phase boundary (MPB) -- setting -- piezo-electricity, such as a piezoelectric constant (d constant), -- since the property which contributes to a variation rate improves, as a charge of actuator material, the piezoelectric-ceramics ingredient of said presentation near the MPB is put in practical use widely.
[0004]
[Problem(s) to be Solved by the Invention] however, the value calculated by the resonance-antiresonance method by which said piezoelectric constant was generally shown in the EMAS-6100 grade -- it is -- fundamental -- the piezo-electricity at the time of low electric-field (divisor 100 V/m extent) impression -- the rate of a variation rate is shown. On the other hand, the drive electric field in an actual electrostrictive actuator may also become hundreds kV/m - thousands kV/m, and may not have semantics with the practical piezoelectric constant for which it asked by said approach. Furthermore, in connection with the breadth of the electrostrictive actuator use range, the property stability in a large temperature requirement, especially the temperature stability of electrostatic capacity are called for in recent years. For example, when an electrostrictive actuator is used as components for automobiles, according to the operating environment, the property stability in the large temperature requirement which also becomes -40 degrees C - 170 degrees C may be required. On the other hand, generally, temperature fluctuation of specific inductive capacity became large, and the problem has produced the piezoelectric-ceramics ingredient in said presentation near the MPB at the stability of the actuator property in a large temperature requirement, especially the stability of electrostatic capacity.
[0005] Since d constant is large, the piezoelectric-ceramics constituent of $PbTiO_3$-$PbZrO_3$-Pb(nickel1/3Nb 2/3) O_3 system (it is hereafter called a PNN-PZT system) is used as a piezoelectric-ceramics ingredient for AKUYUETA components.
[0006] However, the ingredient with still bigger d constant is called for as the application range of an electrostrictive actuator spreads. Moreover, the piezoelectric-ceramics ingredient of this system has comparatively small electrical resistivity, like a laminating mold piezoelectric device, when much more thickness uses it for the component around 100 micrometers, the electrical potential difference which can be impressed could not be enlarged, but sufficient property cannot be pulled out or the trouble of carrying out dielectric breakdown during use has produced it.
[0007] Moreover, since the temperature fluctuation of electrical resistivity of said PNN-PZT system piezoelectric-ceramics ingredient was also large, when using it especially in the above large temperature requirements, it had the problem of dependability falling further.
[0008] Then, it is to offer the piezoelectric-ceramics constituent excellent in insulation while the piezo-electric distorted constant at the time of high-voltage impression of 1 technical technical problem of this invention is large, and its

temperature change of specific inductive capacity is small and it has a stable property greatly [the electrical resistivity in the high temperature range] therefore in a large temperature requirement.

[0009] Moreover, the special technical technical problem of this invention is to offer a piezoelectric-ceramics constituent very useful as a charge of actuator material.

[0010]

[Means for Solving the Problem] As a result of investigating various properties, the presentation range is located to a predetermined field. the piezo-electricity of the piezoelectric-ceramics constituent by which this invention person is expressed with empirical formula $aPbTiO3+bPbZrO3+CPb(nickel1/3Nb 2/3) O3$ (a+b+c=100) -- a variation rate -- the amount of Pb(s) -- **** -- **** -- by adding alkaline earth elements, such as lanthanoidses, such as things, and La, Nd, and Sr, as an accessory constituent, when the direct-current electric field of 500 kV/m are impressed in the same direction as a polarization shaft ****** displacement (the following, d33 (500kV)) has improved from the case of only a mother component, and degradation of the temperature change of the specific inductive capacity in the range of -40 degrees C - 170 degrees C found out few piezoelectric-ceramics constituents. Moreover, it comes to succeed that the insulation of a piezoelectric-ceramics constituent improves in a header and this invention by converting Mn into the oxide expressed with MnO to the piezoelectric-ceramics ingredient of the above-mentioned publication, and containing at a 0 - 0.05wt% (0 not containing) rate.

[0011] According to this invention, it is expressed with empirical formula $aPbTiO3+bPbZrO3+cPb(nickel1/3Nb 2/3) O3$ (a+b+c=100). The presentation range Namely, I points of drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), In the same direction as the polarization shaft which the range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points was used [shaft] as the mother component, and decreased the amount of Pb(s) in [0-3 mol] % (except for 0), and the direct-current electric field of 500 kV/m the piezo-electricity when impressing -- the piezoelectric-ceramics constituent which a variation rate shows 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in the range of -40 degrees C - 170 degrees C is obtained.

[0012] Moreover, according to this invention, it sets to said piezoelectric-ceramics constituent. As opposed to a mother component At least one sort in alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, is added in [0-7 mol] % (except for 0). In **** the amount of Pb(s) in the same direction as **** and a polarization shaft in [0-5 mol] % (except for 0) the direct-current electric field of 500 kV/m the piezo-electricity when impressing -- the piezoelectric-ceramics constituent which a variation rate shows 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in the range of 40 degrees C - 170 degrees C is obtained.

[0013] According to this invention, it is expressed with empirical formula $aPbTiO3+bPbZrO3+cPb(nickel1/3Nb 2/3) O3$ (a+b+c=100). The presentation range Moreover, I points of drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), The range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points is used as a mother component. Among alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, and one or more kinds A variation rate shows 500 or more pm/V. the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as the polarization shaft added in [0-5 mol] % (except for 0) -- in -40 degrees C - 170 degrees C The piezoelectric-ceramics constituent characterized by the temperature change of specific inductive capacity being 300% or less is obtained.

[0014] Moreover, according to this invention, in said one of piezoelectric-ceramics constituents, Mn is converted into the oxide expressed with MnO to a total amount, it contains at a 0 - 0.05wt% (0 does not contain) rate, and the piezoelectric-ceramics constituent characterized by the specific resistance in -40 degrees C - 170 degrees C being 1.0x1011 or more ohm-cm is obtained.

[0015]

[Embodiment of the Invention] First, it explains, referring to a drawing about the piezoelectric-ceramics constituent of this invention.

[0016] Drawing 1 is drawing showing the presentation of the mother component of the piezoelectric-ceramics constituent of this invention by the triangular coordinate.

[0017] The piezoelectric-ceramics constituent of this invention is expressed with empirical formula $aPbTiO3+bPbZrO3+cPb(nickel1/3Nb 2/3) O3$ (a+b+c=100). The presentation range I points of drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), The range made into the field surrounded by the line top which connects K points (a= 50-mol% and b= 40-mol% and c= 10-mol%) and each L

forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points is used as the mother component.

[0018] piezo-electricity when an example of the piezoelectric-ceramics constituent of this invention impresses the direct-current electric field of 500 kV/m in the same direction as a polarization shaft by decreasing the amount of Pb(s) in [0-3 mol] % (except for 0) from this mother component -- a variation rate shows 500 or more pm/V, and the range of it is -40 degrees C - 170 degrees C, and it is the piezoelectric-ceramics constituent which the temperature change of specific inductive capacity made 300% or less.

[0019] Moreover, another example of the piezoelectric-ceramics constituent of this invention said piezoelectric-ceramics constituent -- setting -- a mother component -- receiving -- the inside of alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, -- at least one sort -- the 0-7-mol range of % (except for 0) -- adding -- and the amount of Pb(s) -- the 0-5-mol range of % (except for 0) -- **** -- **** -- by things the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as a polarization shaft -- a variation rate shows 500 or more pm/V, and the range of it is 40 degrees C - 170 degrees C, and it is the piezoelectric-ceramics constituent which the temperature change of specific inductive capacity made 300% or less.

[0020] The piezoelectric-ceramics constituent of this invention further moreover, another example By adding one or more kinds in alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, in [0-5-mol] % (except for 0) to a total amount for said mother component the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as a polarization shaft -- it is the piezoelectric-ceramics constituent a variation rate shows 500 or more pm/V, and the range of it is -40 degrees C - 170 degrees C and whose temperature change of specific inductive capacity is 300% or less. [whose]

[0021] Moreover, while another example of the piezoelectric-ceramics constituent of this invention adds at least one sort in alkaline earth elements, such as lanthanoidses, such as La and Nd, and Sr, in [0-7 mol] % (except for 0) to a total amount to said mother component A variation rate shows 500 or more pm/V. the amount of Pb(s) -- the 0-5-mol range of % (except for 0) -- **** -- **** -- the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as a polarization shaft by things -- in 40 degrees C - 170 degrees C The temperature change of specific inductive capacity is the piezoelectric-ceramics constituent which is 300% or less.

[0022] Moreover, in said one of piezoelectric-ceramics constituents, other examples of the piezoelectric-ceramics constituent of this invention convert Mn into the oxide expressed with MnO to a total amount, are made to contain it at a 0 - 0.05wt% (for 0 not to contain) rate, and are piezoelectric-ceramics constituents whose specific resistance in -40 degrees C - 170 degrees C is 1.0×10^{11} or more ohm-cm.

[0023] Then, the gestalt of operation of this invention is explained.

[0024] (Gestalt of the 1st operation) Weighing capacity of the lead oxide (PbO) which carried out the amount reduction of Pb(s) with the raw material of titanium oxide (TiO_2), a zirconium dioxide (ZrO_2), nickel oxide (NiO), and niobium oxide (Nb $2O_5$) was carried out so that it might become a target system, and with the zirconia ball, such raw material powder was put in into the acrylic pot, and carried out wet blending for 20 hours.

[0025] Next, after performing **** for such mixed powder in alumina ****** after dehydration desiccation, wet grinding of each ****** was carried out with the zirconia ball in an acrylic pot for 15 hours. Then, the binder was mixed to the **** pulverized powder obtained by carrying out dehydration desiccation, it was pressurized, and it fabricated to diameter (phi) 20x thickness (T)3mm. After calcinating this Plastic solid at 1100 degrees C - 1300 degrees C for 2 hours and processing each sintered compact into the thickness of 1mm, it considered as the sample from which a presentation differs, respectively by applying a silver paste to both sides, being burned on them at 450 degrees C, and forming an electrode in them. thus, it came out of 3kV /of each obtained sample mm, polarization processing was carried out, HP4194A and a thermostat were used, and the 1kHz temperature characteristic of specific-inductive-capacity epsilonr was measured. After holding the temperature characteristic 5 degrees C - every 10 degrees C in -40 degrees C - 400 degrees C for 30 minutes, it measured 1kHz epsilonr in each temperature. Moreover, d33 (500kV) impressed the electrical potential difference of OV->500V ->0V to said sample supported in the central point in uniform velocity and 2 seconds, and measured and computed the variation rate of the sample thickness direction using the fringe counter type laser displacement gage.

[0026] Drawing 2 is drawing showing the example of measurement of d33 (500kV). it is shown in drawing 2 -- as -- a test portion with a thickness of 1mm -- the variation rate at the time of direct-current-voltage impression of 500V (field strength 500 kV/m) -- d33 (500kV) was computed from the amount.

[0027] Moreover, the rate of a temperature change of a mother component, d33 (500kV) of Pb reduction ingredient, and -40 degrees C - 170 degrees C epsilonr is shown in the samples 1-26 of the following tables 1 and 2. Sample No. which front Naka and * attached shows the outside of the range of this invention.

[0028] The following things can be read from the above-mentioned table 1. That is, improvement in d33 (500kV) is accepted, maintaining the temperature characteristic by decreasing the amount of Pb(s). As for the improvement in d33 (500kV), Pb decrement falls gradually as with a peak of about 1.5mol%. If Pb decrement becomes superfluous, the degree of sintering of a sample will begin to fall, and elevated-temperature-izing of sintering temperature and property degradation of a sample generate and are not desirable. sample No. -- since the value of d33 (500kV) becomes less than 500 pm/V, 25 and 26 are not contained in the range of this invention, respectively. As for the property made into the target of this invention, these results show that Pb decrement is attained in [0-3 mol] % (0 removes).

[0029] A lead oxide (PbO), titanium oxide (TiO2), (Gestalt of the 2nd operation) As a zirconium dioxide (ZrO2), nickel oxide (NiO), and the mother component raw material and additive element of niobium oxide (Nb 2O5), a lanthanum trioxide (La 2O3), Weighing capacity of oxidization neodium (Nd 2O3) and the strontium carbonate (SrCO3) was carried out so that it might become the purpose presentation, and evaluation of creation and many properties was performed for the sample like the gestalt of the 1st operation.

[0030] The rate of a temperature change of -40 degrees C - 170 degrees C epsilonr is indicated to be d33 (500kV) of an additive sample to sample No.27-39 of following Table 1 and 2. Sample No. which the following table 1 and * in Table 2 attached shows the outside of the range of this invention. The following things can be read from the following table 1. That is, while improvement in d33 (500kV) is accepted according to the increment in the amount of additives in each element, the value of deltaepsilonr deteriorates. Since deltaepsilonr is over 300%, sample No.30 which added Sr superfluously are excepted from this generic claim. Moreover, during sample creation, were able to damage sample No.39 and they were not able to be measured.

[0031] A lead oxide (PbO), titanium oxide (ZrO2), (Gestalt of the 3rd operation) As a zirconium dioxide (ZrO2), nickel oxide (NiO), and the mother component raw material and additive element of niobium oxide (Nb 2O5), a lanthanum trioxide (La 2O3), Weighing capacity of oxidization neodium (Nd 2O3) and the strontium carbonate (SrCO3) was carried out so that it might become the purpose presentation, and evaluation of creation and many properties was performed for the sample like the gestalt of the 1st operation. The rate of a temperature change of -40 degrees C - 170 degrees C epsilonr is indicated to be d33 (500kV) of a sample to sample No.40-64 of the following table 2. Sample No. which * in Table 2 attached shows the outside of the range of this invention. The following things can be read from the following table 2. A lot of additives can be added and there is less degradation of deltaepsilonr than the case where the amount of Pb(s) is simply added by decreasing with addition of an additive. moreover, sample No. which added Pb decrement and the addition and maintains about 0.99-mol balance -- in 42, 47, and 54 grades, an addition shows d33 [good comparatively at least] (500kV).

[0032]

[Table 1]

備考	試料 No.	各 成 分			Pb 減少量 /mol%	添加物	d₃₃(500KV) /pm·V⁻¹	Δεr/%
		a	b	c				
*	1	43	12	45	−	−	530	500
*	2	44	16	40	−	−	670	170
*	3	39	21	40	−	−	1250	650
*	4	50	15	35	−	−	450	170
*	5	45	20	35	−	−	530	180
*	6	40	25	35	−	−	1000	230
*	7	35	30	35	−	−	800	280
*	8	30	35	35	−	−	700	700
*	9	47.5	30	22.5	−	−	520	160
*	10	37.5	40	22.5	−	−	750	290
*	11	55	35	10	−	−	470	150
*	12	50	40	10	−	−	520	160
*	13	45	45	10	−	−	700	170
*	14	40	50	10	−	−	600	270
*	15	35	55	10	−	−	520	700
*	16	51	44	5	−	−	420	160
*	17	46	49	5	−	−	480	190
*	18	41	54	5	−	−	400	280
	19	47.5	30	22.5	0.5	−	714	160
	20	47.5	30	22.5	1	−	811	160
	21	47.5	30	22.6	1.5	−	805	160
	22	47.5	30	22.6	2	−	717	150
	23	47.5	30	22.5	2.5	−	649	160
	24	47.5	30	22.5	3	−	570	170
*	25	47.5	30	22.6	4	−	306	180
*	26	47.5	30	22.6	5	−	283	170
	27	43	34.5	22.5	−	1.0mol%Sr	950	210
	28	43	34.5	22.5	−	3.0mol%Sr	1050	220
	29	43	34.5	22.5	−	5.0mol%Sr	1010	270
*	30	43	34.5	22.5	−	7.0mol%Sr	900	470
	31	43	34.5	22.5	−	0.05mol%Nd	1000	210
	32	43	34.5	22.5	−	0.1mol%Nd	935	200

＊本発明の範囲外

[0033]
[Table 2]

備考	試料 No.	各成分 a	b	c	Pb減少量 /mol%	添加物	d_{33}(500KV) /pm·V⁻¹	Δεr/%
	33	43	34.5	22.5	—	0.3mol%Nd	1150	230
	34	43	34.5	22.5	—	0.5mol%Nd	980	300
	35	43	34.5	22.5	—	0.1mol%La	980	210
	36	43	34.5	22.5	—	0.3mol%La	980	210
	37	43	34.5	22.5	—	0.5mol%La	1080	210
	38	43	34.5	22.5	—	1.0mol%La	860	270
*	39	43	34.5	22.5	—	2.0mol%La	測定不可	測定不可
	40	43	34.5	22.5	1	0.1mol%La	1050	210
	41	43	34.5	22.5	1	0.3mol%La	1080	230
	42	43	34.5	22.5	1	0.5mol%La	1180	220
	43	43	34.5	22.5	2	0.1mol%La	1000	200
	44	43	34.5	22.5	2	0.3mol%La	1040	220
	45	43	34.5	22.5	2	0.5mol%La	1080	240
	46	43	34.5	22.5	1	0.05mol%Nd	1080	210
	47	43	34.5	22.5	1	0.1mol%Nd	1120	220
	48	43	34.5	22.5	1	0.3mol%Nd	1050	240
	49	43	34.5	22.5	2	0.05mol%Nd	1130	220
	50	43	34.5	22.5	2	0.1mol%Nd	1110	220
	51	43	34.5	22.5	2	0.3mol%Nd	1040	270
	52	43	34.5	22.5	1	1.0mol%Sr	970	200
	53	43	34.5	22.5	1	3.0mol%Sr	1000	210
	54	43	34.5	22.5	2	1.0mol%Sr	1060	210
	55	43	34.5	22.5	2	3.0mol%Sr	1050	220
	56	43	34.5	22.5	2	5.0mol%Sr	1080	260
	57	43	34.5	22.5	3	1.0mol%Sr	1010	200
	58	43	34.5	22.5	3	3.0mol%Sr	1040	210
	59	43	34.5	22.5	3	5.0mol%Sr	1100	270
	60	43	34.5	22.5	4	3.0mol%Sr	1150	210
	61	43	34.5	22.5	4	5.0mol%Sr	1200	260
	62	43	34.5	22.5	5	3.0mol%Sr	1120	210
	63	43	34.5	22.5	5	5.0mol%Sr	1100	250
	64	43	34.5	22.5	5	7.0mol%Sr	1000	300

＊印は本発明の範囲外

[0034] A lead oxide (PbO), titanium oxide (TiO2), (Gestalt of the 4th operation) As a zirconium dioxide (ZrO2), nickel oxide (NiO), and the mother component raw material and additive element of niobium oxide (Nb 2O5), a lanthanum trioxide (La 2O3), Weighing capacity of oxidization neodium (Nd 2O3), a strontium carbonate (SrCO3), and the manganese carbonate (MnCO3) was carried out so that it might become the purpose presentation, the sample was created like the gestalt of the 1st operation, and -40 degrees C of specific resistance which comes out 170 degrees C, respectively were measured. An example of the result is shown in underline drawing 3. the constant temperature from drawing 3 -- in a field, although specific resistance falls, it turns out that specific resistance improves notably and is satisfied only with carrying out ultralow volume addition of MnCO3 as MnO of the desired value of this invention. Moreover, when the addition of MnO exceeded 0.05wt%, it turned out that the improvement effectiveness in specific resistance beyond it can be desired, and there is nothing. For a certain reason, superfluous addition of MnO can also judge the inclination to degrade piezo-electric properties, such as a piezoelectric constant, that less than [0.05wt%] is a suitable value to the target of this invention.

[0035]
[Effect of the Invention] As explained above, while having a stable property in this invention in a large temperature requirement from the piezo-electric distorted constant at the time of high-voltage impression being large, and the temperature change of specific inductive capacity being small, and the electrical resistivity in the high temperature range being large, the piezoelectric-ceramics constituent excellent in insulation can be offered, and it is very useful as a charge of actuator material.
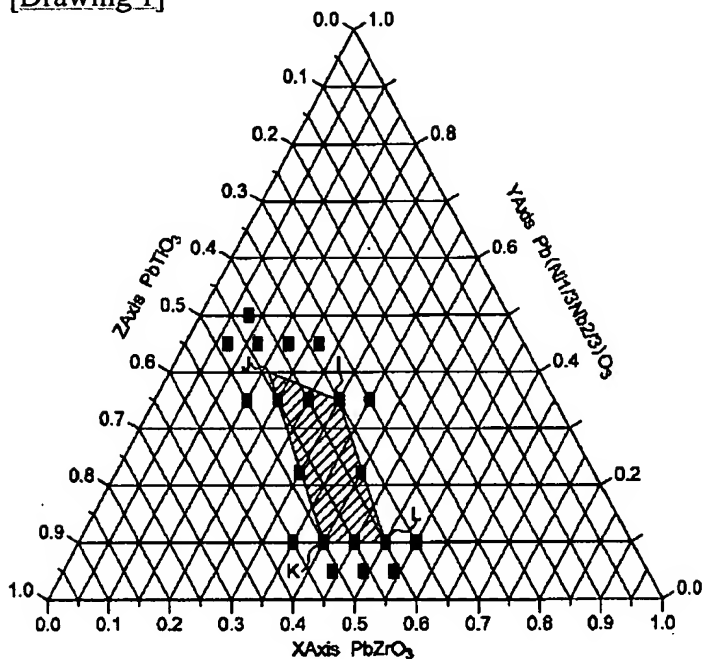
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* NOTICES *

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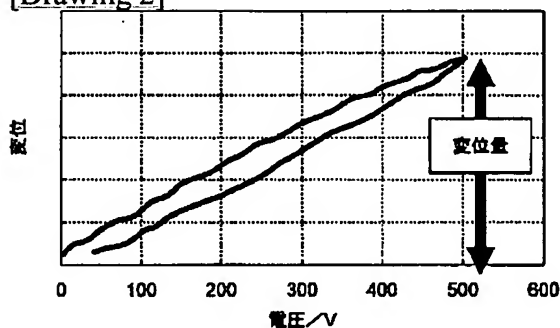damages caused by the use of this translation.**

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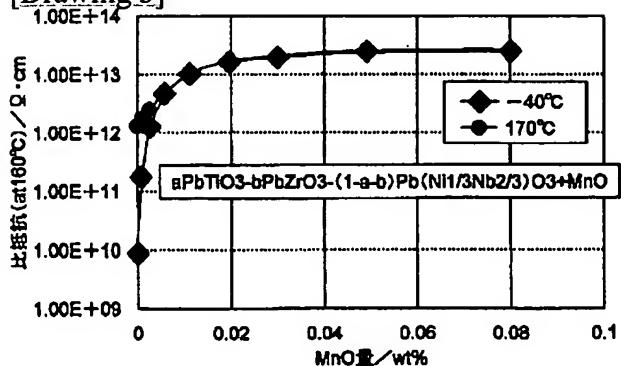3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

[Drawing 2]

[Drawing 3]

[Translation done.]